FLUORESCENCE IN GEOLOGY

A THESIS

PRESENTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

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ABSTRACT

Fluorescence is defined as the emission of visible light by a substance under the influence of an exciting agent. Ultraviolet radiation is the most common exciting agent. Fluorescence is explained on the molecular level as an absorption of energy by electrons which subsequently jump to higher energy levels. From this unstable state they lose energy in the form of heat and upon returning to their former energy levels, emit radiation in the form of visible light. However, there are many factors, in the ultraviolet source, in the specimen itself, and in the receptor of the fluorescence, which can effect the intensity and the color of the fluorescence. Fluorescence finds employment in such diverse fields as analysis and prospecting. Color fluorescent photography can be used to permanently record the fluorescent phenomenon but some means of color control must be developed to obtain color-true prints.

INTRODUCTION AND HISTORY

Luminescence is the general term applied to an emission of light. Two kinds of luminescence have been recognized. The first, candoluminescence, is the direct result of temperatures in excess of 1000° C. The second type, fluorescence, is virtually a cold process. It is with this latter phenomenon that this report is mainly concerned.

Fluorescence is defined as the emission of visible light by a substance under the influence of an exciting agent. Certain substance fluoresce when

bombarded by gamma rays, x-rays, visible light, or electrical waves. Still others emit light when excited by some change in their physical surroundings; this may be such factors as an increase in pressure, or a decrease in temperature. However, ultraviolet radiation is commonly used to induce fluorescence for several practical reasons (i.e., relatively inexpensive and safe, easier to produce and control, and affects a greater variety of substances). Ultraviolet radiation is therefore the exciting agent used to produce the results described in this report.

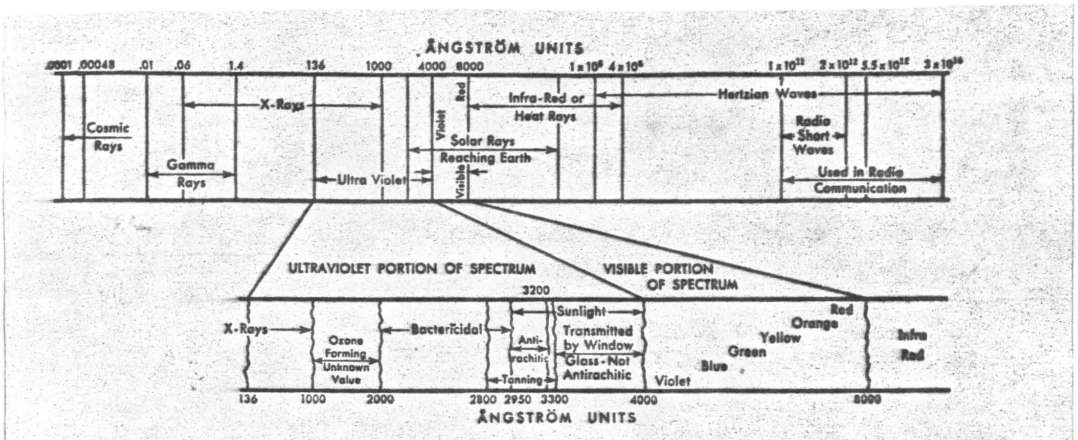
V. Cascariola, a cobbler and alchemist living in Bologna, Italy, is credited with the first discovery of fluorescence (excited by the ultraviolet rays inherent in natural sunlight) in a calcined mineral substance he collected on the outskirts of Bologna. His" Bologna Stone" became a standard tool of the seventeenth century alchemist. Modern mineralogy has identified it as barite.

Scientific developments began with Sir David Brewster in 1833 when he studied the ultraviolet portion of sunlight. In 1852, Sir George Stokes suggested the term "fluorescence" to replace the phrase "true inner dispersion" used by Brewster. Stokes chose this term since the fluorite specimens he was studying exhibited this phenomenon so markedly. Stokes is credited with laying the foundation for modern investigation of fluorescence.

GENERAL THEORY

In explaining fluorescence it is necessary to first examine the Bohr model of the atom. Simply stated, an atom consists of electrons revolving about a nucleus in different orbits or energy levels. The farthest removed orbits are known to have the most kinetic energy.

An understanding of Planck's concept of the nature of radiant energy is also required in explaining fluorescence. Planck proposed that visible light and other forms of electromagnetic radiation are transmitted in small specific units known as photons. It is also understood that ultraviolet radiation is very similar to light in the visible part of the spectrum (refer to figure 1) except that it is of shorter wavelength. Planck's investigations also revealed that ultraviolet photons have more energy then photons of visible light.



THE ELECTROMAGNETIC SPECTRUM

Showing the position of ultraviolet radiations and the range of human vision as measured in Ångström Units. The exact nature and actions of the radiations between 1000 and 2000 A. U. is not known with certainty.

Figure 1- The Electromagnetic spectrum. (after DeMent, 1945) See text for discussion.

It is now possible to postulate what happens when a stream of ultraviolet photons strikes an atom of a fluorescent substance. The amount of energy carried by the photons is just enough to force some of the electrons of the atom into an outer orbit, or a higher energy state.

These transposed electrons are now in a more or less unstable state and soon fall back to their former energy levels. In so doing they emit a quantum of energy. Since some of the energy delivered by the ultraviolet photons has been lost in the form of heat, the emitted unit has less energy then the one which entered. This means that it must have a longer wavelength and is therefore more towards the red end of the spectrum. This emitted radiation usually falls within the range of wavelengths detectable by the human eye.

Early investigators soon discovered that pure substances would not fluoresce. Thus, the necessity of some activating agent was deducted. Refined chemical analysis has revealed the activator in most fluorescent minerals. It is to be noted that the impurity which is responsible for the coloration of a mineral in natural light is not necessarily the impurity which is acting as the fluorescent activator. Also the activating impurity may be present in such minute quantities that the mineral appears colorless in natural light. Some clear diamonds which fluoresce yellow under ultraviolet radiation are good examples of this.

Manganese and the rare earth elements are by far the most common activators. Gunnell, 1935, states that the rare earth elements are the activating impurities in all specimens of fluorescent fluorite. Dake and DeMent, 1941, state that some connection, direct or indirect, with manganese can

usually be traced. For example, it has been shown that the red fluorescence of some calcite is directly dependent upon the manganesecontent of the calcite. Calcite with about 3.5% manganese appeared to give a maximum brilliance; the fluorescence declining gradually with a greater manganese content, reaching zero with the presence of about 17% manganese. This reduction in the intensity of the fluorescence when the concentration of the activator passes a certain optimum has been found to hold true in nearly all cases. There is also evidence that the presence of iron and magnesium in calcite tends to act as inhibitors to fluorescence.

To understand the role of the activator in fluorescence, it is necessary to re-examine the energy levels of an atom. In figure 2, F represents the normal zone or energy level of an electron under unexcited conditions. E represents a normally empty energy level to which the electron would be raised if excitation could be brought about. When L, a localized state, is interspersed between the normally filled and normally empty zones, as when an activating agent is added, the mechanism changes. Part of the energy states of the activator will overlap with the top of the normally filled zone. It is also possible to obtain an activator which will cause the top filled energy level to appear as a discrete, localized state superimposed on the normally filled zone. Thus, a bridge is provided by the activator between zones F and E.

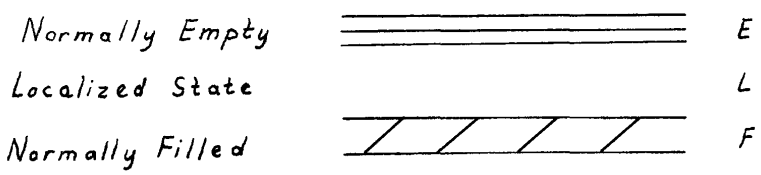


Figure 2 - Electron Zones in a fluorescent atom. (after DeMent, 1945) Refer to text for explanation.

The relative stability of the electron when forced into the higher energy level determines whether or not a mineral will be phosphorescent, that is, whether it will continue to emit radiation after the exciting radiation is stopped. It is thought that phosphorescence is more likely to occur in crystals in which the space lattices are distorted by different kinds of impurities. In this case the electrons may be ejected from the atom completely and the light given off by some other atom which captures them.

VARIABILITY

A fluorescent specimen may appear bright red to one investigator and a mild pink to another. Someone else may not be able to detect a weak fluorescence in a certain mineral as reported by a colleague. This variability in what is perceived as fluorescence by the eye or by the camera is an important characteristic of fluorescence neglected by most observers. There are three main sources from which variability in intensity or color of the fluorescence of a mineral may be incurred. First, variability may be introduced by the ultraviolet source; second, by the physical state of the observed specimen; and third, by the abilities and nature of the receptor of the fluorescence.

More specifically, the emission characteristics of the ultraviolet light (i.e., wavelength and intensity of rays) is obviously directly related to the nature of the resulting fluorescence. Perhaps the biggest problem along this line arises from the many different types of ultraviolet units available. It is to be expected that, for example, willemite from Franklin, New Jersey, looks

different under a high intensity quartz tube lamp as opposed to a black bulb type lamp. However, seldom is this basic fact, type of unit used, stressed in the literature.

Even among the same types of lamps the wave length may vary for a variety of reasons and therefore excite a specimen to a different degree. Such factors as available voltage and the heat at which the bulb burns, which are in turn affected by the length of the electrical cord and the age of the bulb, may combine effects to have an undeniable place for consideration in quantitative, scientific investigations.

Another type of problem arises from the filters used in all ultraviolet sources. These filters commonly vary both in type and efficiency of transmission. Since there is no "perfect filter" some amount of the visible spectrum is passed from all ultraviolet sources. This visible light (mainly purple and some red) may not only overshadow the delicate blue and lavender of some fluorescence, but it may produce new additive colors with the true fluorescence.

A final consideration related to the ultraviolet source itself involves the distance from the source to the specimen. Intensity of fluorescence increases with increasing intensity of the ultraviolet light (Dake, 1942) and this is affected by the lamp to sample distance. In any quantitative investigations this factor must also be taken into consideration.

The second major source of variability is concerned with the physical state of the observed specimen. Specifically, factors such as the temperature of

the specimen and the pressure exerted upon it influence its' fluorescence. Kröger, 1948, states that increasing temperature causes the crystal lattice to increase in size without changing in form. There is a corresponding loss of fluorescence which will return, unimpaired upon cooling. It has also been noted that different stages of pulverization may effect the fluorescence of some minerals.

As most geologists would expect, the degree of weathering of the specimen examined may effect the results obtained. However, in at least one case, the geologist who studies only the fresh, unweathered specimen may overlook a valuable clue. Although pitchblende (uraninite) does not itself fluoresce, it commonly developes a coating of alteration products which may fluoresce a strong yellow-green. This is more fully discussed in a following section of geologic applications.

The third major source of variability in observed fluorescence is in the abilities and nature of the receptor. The receptor is either the human eye, various scientific measuring devices, or a camera.

Often the variability of fluorescence depends on the observer. Reception to radiation of different wavelengths vary for persons of different ages. Radiation at about 3800 A.U. is visible to most persons between 15 and 30 years of age, but many older persons can see only down to about 3950 A.U. Color blindness, fatigue, carelessness, inexperience and fluorescence of the eye itself in reflected ultraviolet light also lead to variation in perception.

Since instruments like the spectrograph and photometer are not ordinarily available to the general observer, words are depended upon to describe fluorescence. Their subjective nature and lack of standards leads to some ambiguity in the literature on fluorescence.

The third major receptor of fluorescence is the camera. All the complexities and problems of color-true fluorescent photography are discussed in a following section.

GEOLOGIC APPLICATIONS OF FLUORESCENCE

The geologist is really just discovering the utility of fluorescence. However, he is not slow to learn and the ultraviolet light is changing from a novelty and toy to a basic tool. There are three major fields of application of fluorescence in geology. These are as an aid in identification of minerals, as a tool of the mining industry in prospecting, and as a new and exciting tool of the petroleum industry.

The first use of fluorescence listed above is in the identification of minerals, this is termed fluorescence analysis. It was formerly assumed to be entirely subjective. However, DeMent (1942) states that quantitative fluorescent analysis is now as objective and exacting as spectoscopy. Exacting devices, such as the photometer and the spectrograph, used in physics and chemistry for measurements of radiation have been adapted into fluorometers and fluorephotometers and the result has been to increase the scope and accuracy of fluorescent identification.

The mining industry is one of the principal users of fluorescence. For years the zinc mining industry around Franklin, New Jersey, has exploited the phenomenal fluorescence of both the primary ore mineral (willemite) and the gangue mineral (calcite). Surveying at night or in a mine with a portable ultraviolet light unit

is quick, easy, and inexpensive. Ultraviolet lights are employed to aid in the milling process of the ore and to check the quality of the recovery process. Much of the same may be said of the tungsten industry and the fluorescence of the tungsten ore, scheelite. An ultraviolet light in the hands of an experienced person can be used for quick and inexpensive assays which prove amazingly accurate.

As mentioned earlier, the uranium ore, pitchblende, may weather to a fluorescent alteration product and this fact may be cautiously employed in uranium prospecting. However, radioactive prospecting is generally preferred since it is more definite. The ultraviolet test is inconclusive since the pitchblende may simply have weathered to one of the non-fluorescent alteration products.

The third important field of application is found in the petroleum industry. Blau, 1943, found that a subterranian oil pool imparts a characteristic fluorescence to the overlying soil. Actually, the oil itself does not reach the surface, but hydrocarbon gases from the pool commonly diffuse upward through the soil. Certain microorganisms (bacteria) assimulate these gases with a resulting fluorescent end-product. These bacteria can be distinguished from normal soil bacteria since they can be found below the horizon of normal organic decay products. However, a technique of fluorescent prospecting for oil has not yet been developed which can challenge the conventional exploratory techniques used today.

Fluorescent analysis is used by the petroleum industry to determine the grade and purity of both crude and refined oils. John Melhase, 1935, proposed using the fluorescent properties of crude oil as a means of correlating oil sands from one well to another. Melhase observed that no two oils fluoresced in an identical manner unless derived from the same oil-bearing sand. Neither the gravity of the oil, percent of water or mud present, or the manner in which the sample was obtained had any effect upon the fluorescent properties of the oil. Therefore, under properly controlled and regulated conditions, it should be possible to use a fluorescent classification to correlate horizons within an oil field just as fossils are now used. This process of Flurologging may someday provide a new and different means of correlating oil sands.

FLUORESCENCE PHOTOGRAPHY

As shown in figure 1, there are two types of photography involving an ultraviolet light source. In the first, (example 2, figure 3), the visible light produced by the ultraviolet rays striking the specimen is allowed to reach the film whereas the reflected ultraviolet light is stopped by an appropriate filter (e.g., Kokak No. 2 A, 2 B, or skylight filter) in front of the lens. This is by far the most common and useful method which is known as fluorescence photography. The second type, (example 3, figure 3), is different in that only the reflected ultraviolet radiation is allowed to reach the film and the visible light is stopped by an appropriate filter. This is known as ultraviolet light photography.

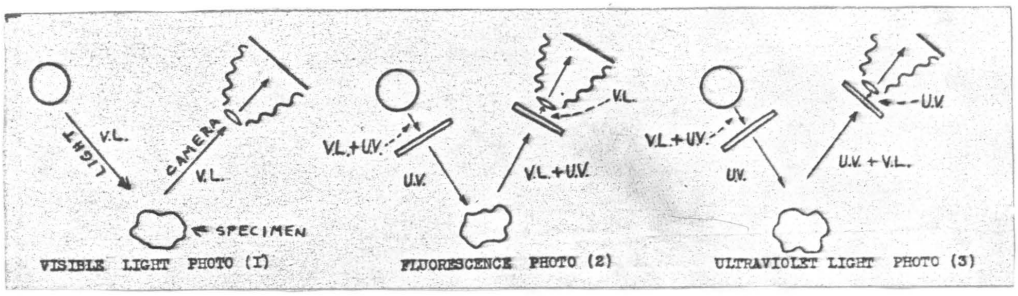


FIGURE 3 Visible Light, Fluorescence, and Ultraviolet Light Photography. (After DeMent, 1943) Refer to text for explanation.

Photographs of minerals in ultraviolet light only, can be made of any mineral irregardless of its' fluorescing capabilities. This may reveal details which cannot be obtained by other photographic methods. For example, it may be necessary to distingish between non-fluorescing particles in a rock which cannot easily be diffentiated under natual lighting. However, possibly due to difficulty in determining correct exposure time, ultraviolet light photography is seldom used.

Fluorescence photography is unusual and in many ways distinctly superior to simple visible light photography since the many advantages inherent in the fluorescent phenomenon are recorded permanently. Many of these advantages are also fairly obvious. For example, details which cannot be seen in ordinary light may often be distinguished and enhanced by their fluorescence or lack of fluorescence; minerals which are apparently identical in white light are frequently shown to be different by fluorescence.

In actual photography of fluorecent objects, complementary filters must be used in the radiation source and in the camera to record the true fluorescent colors. As seen in example 2, figure 3, visible light and ultraviolet light produced by some radiation source is filtered (commonly by an 18 A or ultra-

violet filter) so that only the ultraviolet rays are permitted to strike the specimen. Otherwise the stronger visible light would mask the weaker fluorescence. Upon striking the specimen, some of the ultraviolet light is absorbed and used to create visible light. This is the fluorescence which is recorded on the film. However, some of the ultraviolet rays are reflected from the specimen and since ultraviolet light is stronger photographically than the fluoresced light, the photograph would appear fogged. It is therefore necessary to place a filter (commonly a Kodak No. 2A, 2B, or skylight filter) which removes the ultraviolet and passes the visible radiation. If a filter was not used the reflected ultraviolet radiation could cause the camera lens to fluoresce ruining the photograph. Ordinary lenses are satisfactory in fluorescence photography since they transmit radiation greater than 3,500 A.U. In short wave ultraviolet light photography expensive quartz optics are needed.

For black and white fluorescence photography Kodak suggest their Super Panchro-Press Film, Type B. For color prints, Kodak Ektacolor Film, Type L (long exposure, ASA 64) is recommended instead of the regular Kodacolor Film (ASA 80). Relatively long exposures are common in fluorescent photography and by using the Ektacolor Film, Type L, the chances of running into reciprocity failure are decreased.

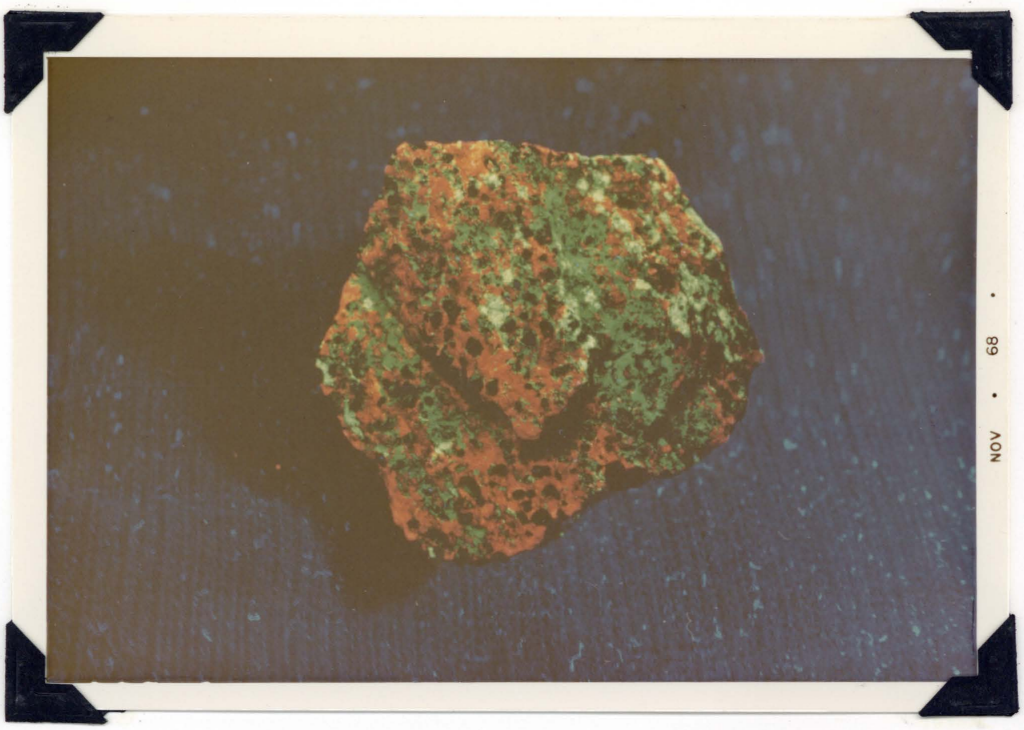
To obtain a color-true photograph, the color printing technician keys on some known color in the photograph. It is therefore a common practice to include the standard Kodak gray card, under the desired lighting conditions, in the first series of photographs taken under that lighting. However, the gray card is useless

in fluorescent photography and there is as yet, no recognized fluorescent substitute. However, when one considers the variabilities discussed in a previous section, exactness of printing techniques seems of minor importance.

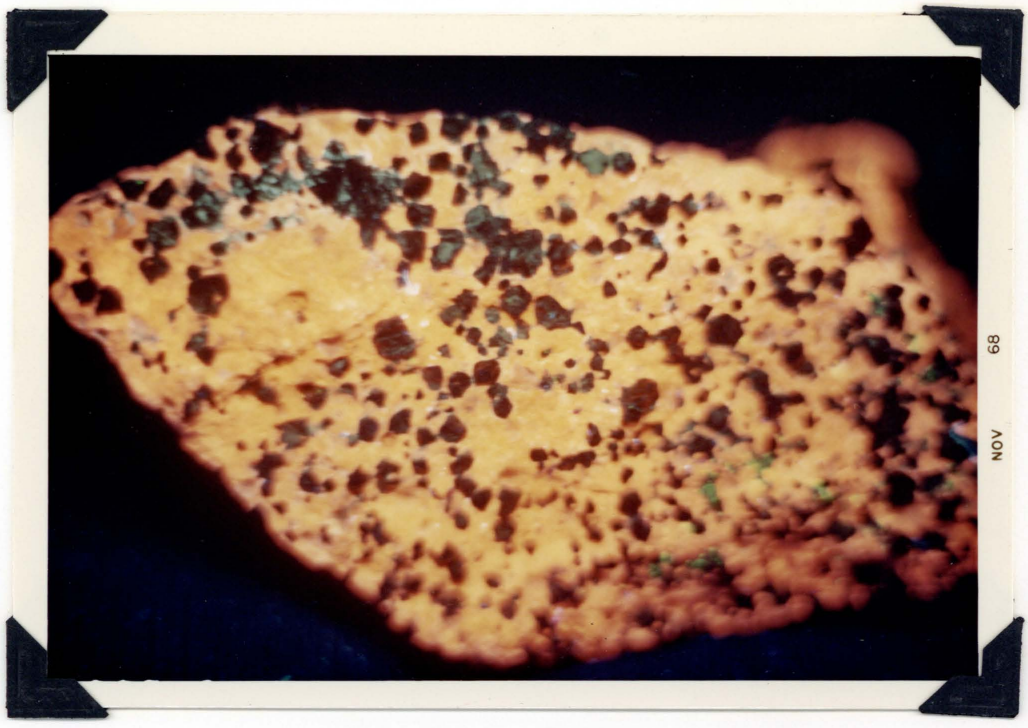
CONCLUSION

There are many factors which may effect the intensity and color of fluorescence produced by ultraviolet radiation. These factors are of crucial importance in such areas as quantitative fluorescent analysis. However, in many fields of application, such as differentiating a fluorescent from a non-fluorescing gangue mineral, these variabilities can usually be ignored. Fluorescence photography provides the obvious advantage of permanently recording the reaction. However, some means of color control must be divised before fluorescence photography can become of greater scientific value.

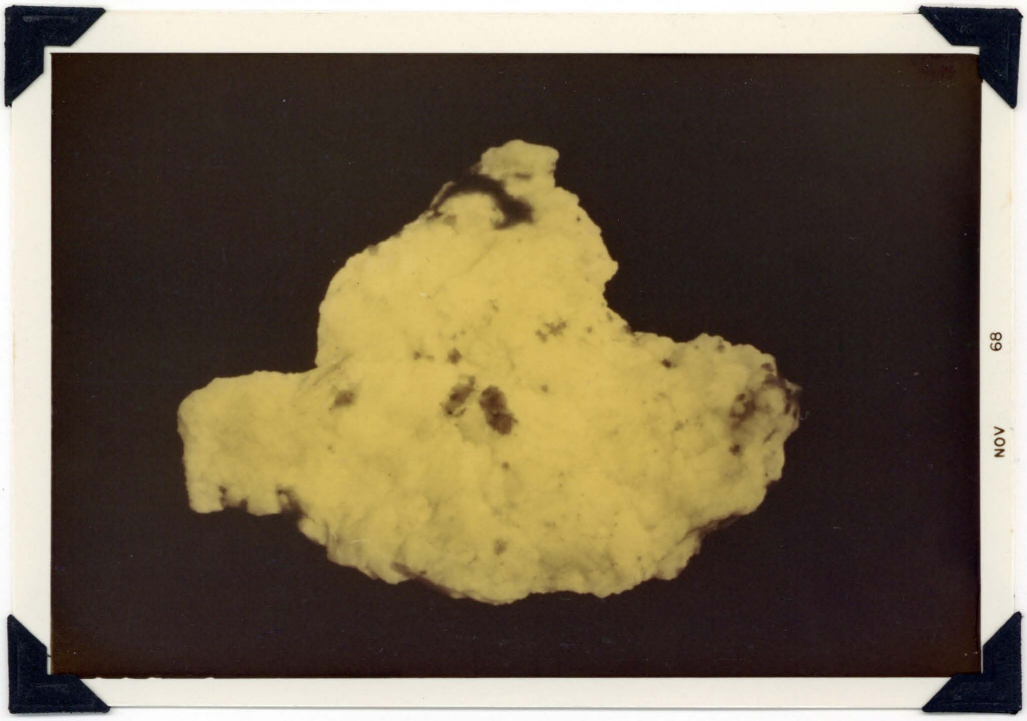
PHOTOGRAPH SECTION



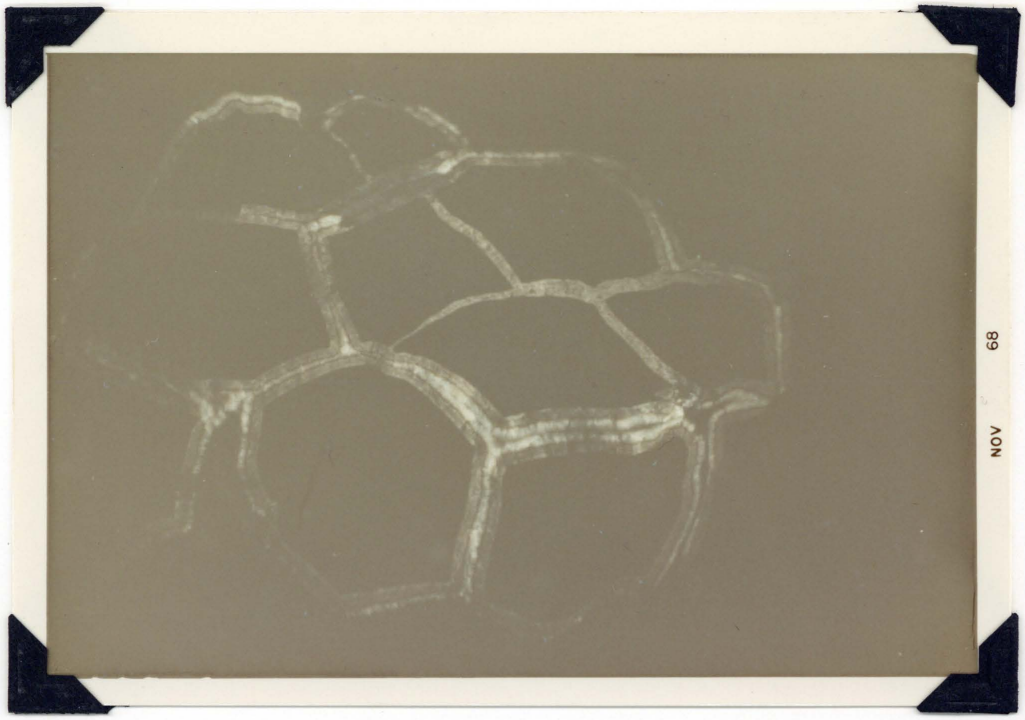
PHOTOGRAPH 1 - Calcite, Willemite, and Franklinite from Franklin, New Jersey. Photograph taken under short-wave ultraviolet radiation. The calcite fluoresced red, the willemite green, the franklinite was non-fluorescent and therefore photographed black. Refer to section on fluorescence at Franklin. (Actual size)



PHOTOGRAPH 2 - Calcite and Franklinite from Franklin, New Jersey. Photograph taken under short-wave ultraviolet radiation. The calcite in this specimen, which appears yellow, actually fluoresced the same red color as in the preceding photograph which is almost color-true. Slight over exposure and the lack of color control resulted in this photographic lie. Refer to the section on fluorescence photography for discussion on color control. (Actual size)



PHOTOGRAPH 3 - Wernertie from Quebec, Canada. Photograph taken under long-wave ultraviolet radiation. This photograph is almost color-true. Under natural light this specimen is pale green with small amounts of brown plagioclase in it. The wernerite may have been derived by alteration from a plagioclase feldspar. (Actual size)



PHOTOGRAPH 4 - A Septarian Concretion from Central Ohio. Photograph taken under long-wave ultraviolet radiation. Note in the wider veins the differentiation of the two "generations" of the cementing calcite. This differentiation is inconspicuous under natural lighting. (Specimen 6 inches by 4 inches)

PHOTOGRAPH 5 - Salt crystalized on sage brush from Salton Sea area of California. Photograph taken under short-wave ultraviolet radiation. Evaporation of brine in an abandoned storage tank resulted in this odd association of salt and sage brush. Under natural light, the salt appears nearly transparent with a red iron stain on the lower portion. This photograph is not color-true since the specimen actually fluoresced a reddish color. (Specimen 6 inches long)

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